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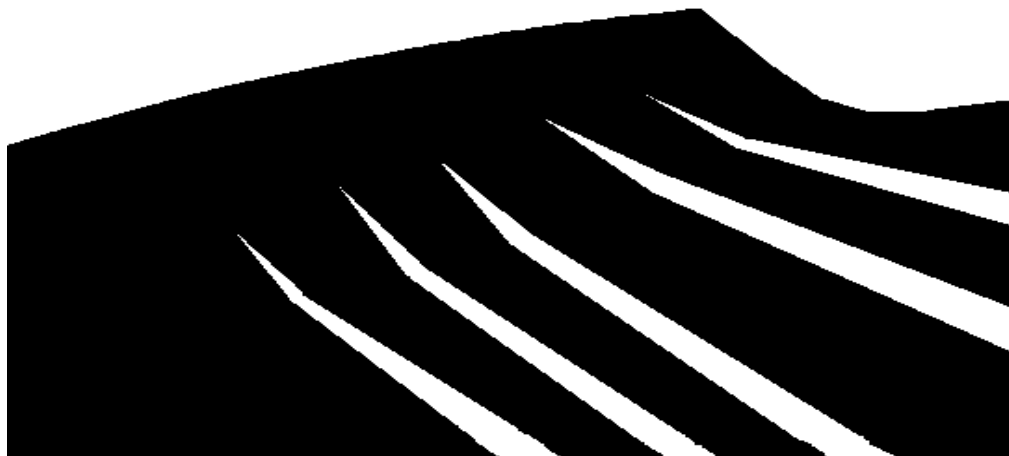
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# USE OF AN ION-SELECTIVE ELECTRODE TO DETERMINE ION CONCENTRATIONS IN SOLUTION

## ***LOS ALAMOS QUALITY PROGRAM***



### APPROVAL FOR RELEASE

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**Los Alamos**  
Yucca Mountain Site  
Characterization Project

## HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	01/18/96	N/A	This procedure supersedes LANL-EES-15-DP-328.
R1	05/06/97	2, 3, 4, 5, 7, 9, 10, 11, & 12	Minor non-substantive editorial changes

**Los Alamos**

Yucca Mountain Site  
Characterization Project

# USE OF AN ION-SELECTIVE ELECTRODE TO DETERMINE ION CONCENTRATIONS IN SOLUTIONS

## 1.0 PURPOSE

This detailed procedure (DP) describes the use of an ion-selective electrode to measure the activity/concentration of an ion in an aqueous solution. This DP is intended to support the C-Wells Reactive Tracer Studies for the Yucca Mountain Project (YMP), although it could also be used for other YMP studies.

## 2.0 SCOPE

This DP applies to any technique in which an ion-selective electrode is used to determine the activity/concentration of an ion in an aqueous solution. It is beyond the scope of this DP to describe and provide instruction for all possible techniques, so the user must document the method used and the results obtained for each application.

## 3.0 REFERENCES

ORION Model 94-35 and 94-53 Halide Electrodes Instruction Manual (1990)  
ORION Model 90-01 single Junction Reference Electrode Instruction Manual (1991)  
ORION Guide to Ion Analysis, Orion Research Inc. (1983)  
ORION pH/mV Meter Instruction Manual, Orion Research Inc. (no date)  
Robinson, R.A. and R.H. Stokes. Electrolyte Solutions, 2<sup>nd</sup> ed., Butterworths, London (1959)  
LANL-EES-4-DP-802, Preparation of Standards for Tracer Concentration Measurements.  
LANL-YMP-QP-02.7, Personnel Training  
LANL-YMP-QP-03.5, Documenting Scientific Investigations  
LANL-YMP-QP-08.1, Identification and Control of Samples  
LANL-YMP-QP-17.6, Records Management

## 4.0 DEFINITIONS

### 4.1 Ion-Selective Electrode

An electrode that, when used in conjunction with a reference electrode, gives a voltage response that is a function of the activity of a specific ion in solution.

## 5.0 RESPONSIBILITIES

The following personnel are responsible for the activities identified in Section 6.0 of this procedure.

- Principal Investigator (PI)
- Procedure User

## 6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this DP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified or replaced by a new document that reflects the current work practice.
- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.
- When this procedure becomes obsolete or superseded, it must be destroyed or marked "superseded" to ensure that this document is not used to perform work.

### 6.1 Principle

An ion-selective electrode, when used in conjunction with a reference electrode and a voltmeter, gives a voltage reading that varies linearly with the logarithm of the ion activity in solution. Ion activities can be measured by a number of different techniques, which can include but are not necessarily limited to (1) direct calibration, (2) known addition, (3) known subtraction, (4) analyte addition, (5) analyte subtraction, and (6) titration. These techniques and their many variations are discussed in detail in the ORION Model 94-35 and 94-53 Halide Electrodes Instruction Manual, the ORION Guide to Ion Analysis, and in many analytical chemistry tests. If the ionic strength of all solutions (i.e., standards, reagents, unknowns) is about the same, electrode responses can be related directly to ion concentrations (see Section 6.4).

### 6.2 Equipment and Hardware/Software

The equipment and hardware/software associated with ion concentration measurements using an ion-selective electrode consists of (1) the electrode(s), (2) a pH meter or voltmeter, (3) devices for adding known weights or volumes or reagents (e.g., pipettes, automatic titrators), and (4) stirring and temperature control devices. The electrode configuration may consist of two physically separate electrodes or a single probe that contains both the working and reference electrodes. The pH meter or voltmeter (e.g., ORION EA 420A pH/mV meter) may be configured to provide direct activity/concentration readings or voltage readings. Stirrers can be mechanical or magnetic depending on the technique used and the sample size. Temperature control can be achieved by a variety of methods, such as a water bath, hot plate, or constant temperature room. Both stirring and temperature control are optional, although significant changes in these variables during a series of measurements should be noted by the user.

#### 6.2.1 Equipment Malfunctions

Malfunctions of any of the equipment described above will be either immediately obvious to the user or will result in the inability to conduct the procedures described in this DP.

#### 6.2.2 Safety Considerations

Safety considerations will depend on the chemical nature of the solutions being analyzed. Material safety data sheets (MSDSs) should be consulted to determine whether special protective clothing and/or eye protection are required. Hazardous chemical wastes should be properly disposed of. Other than the hazards of electrical shock from standard 120 volt electrical outlets and burns if measurements are done at elevated temperatures, there are no hazards associated with the operation of the equipment described above.

#### 6.2.3 Special Handling

Handling of all equipment associated with this DP should be done in accordance with manufacturer's or vendor's guidelines. Special handling of equipment or hardware should be considered on a case-by-case basis as the need arises. Any special handling should be documented in a field or laboratory notebook.

### 6.3 Preparatory Verification

The operation of the electrodes and the pH/voltmeter should be verified by obtaining voltage readings for two standard solutions that differ in ion concentration by as close as possible to a factor of 10. The two readings should differ by  $\frac{60 \pm 5}{n}$  millivolts, where n is the valence of the ion being measured

(the exact difference will depend on the ability to achieve a factor of 10 difference in concentration and a constant temperature). If the electrode is solid state and the response is sluggish, the electrode tip should be polished with aluminum oxide polishing strips and then immersed in the most concentrated standard solution for about 5 minutes before proceeding with calibration or measurements.

#### 6.3.1 Hold Points

NA

#### 6.3.2 Calibration

Calibration is not necessary for some of the techniques used to determine ion activities/concentrations, but when it is necessary, calibration is done before each use per the instruction manual for the ion-selective electrode,

and documented in accordance with QP-03.5. The calibration should be done with a series of standard solutions that span the expected range of concentrations of the unknowns. If possible, the standards should be prepared using the same background solution as the unknowns. If low concentrations are expected, a reading should be obtained for a blank that consists of the unknown solution with no target ion present. This will establish a lower detection limit, and it will also establish whether there are any interfering ions in the solution. Information on interfering ions is generally available in the instruction manual for the ion-selective electrode. Preparation of standards associated with tracer experiments should be done in accordance with DP-802. Alternatively, standard preparation can be documented in a notebook in accordance with QP-03.5.

To check for electrode drift over time, calibrations should be repeated approximately once every hour during a series of measurements. If drift occurs, a new calibration curve should be established and used for subsequent measurements. If the drift exceeds 10 mV (except for a very low concentration standard), the measurements since the last calibration should be repeated.

**NOTE:** The amount of electrode drift that constitutes a significant error can vary considerably depending on the application, the ion being analyzed, the solution composition, and the environmental conditions. As a rule of thumb, a drift of 1 mV constitutes approximately a 4% error for a monovalent ion, and the error becomes larger as ion valence increases.

### 6.3.3 Environment Conditions

Measurements are the most consistent and reproducible when samples and standards are stirred at a constant rate and kept at a constant temperature. However, it may not be practical to achieve these conditions, particularly if the samples are small; so to the extent that these conditions cannot be controlled, the user should record the stirring and temperature conditions during the measurements. If all the standards and unknowns cannot be kept at a constant temperature, they should at least be allowed to experience the same temperature conditions.

**NOTE:** Some pH/voltmeters come with temperature compensating features that allow consistent readings to be obtained even when sample temperatures are not constant. Temperature compensation can be achieved by using a temperature probe connected to the meter or by manually specifying the temperature of each sample. The user should document the use of any of these features.

## 6.4 Control of Samples

Samples are to be identified and controlled in accordance with QP-08.1. All samples should be stored in such a way that evaporation of water is minimized or eliminated during storage (e.g., by storing them in tightly capped bottles, sample refrigeration is not required for samples stored up to one year). The sample container material should be chosen to avoid potential sorption of constituents to the containers walls. If sorption is unavoidable, special procedures should be followed to desorb the tracers prior to analyses (e.g., acidification). These procedures should be documented in a field or laboratory notebook. If there is any question about sorption to container walls, batch sorption experiments should be conducted (and documented in a field or laboratory notebook) using the constituents and labware in question. Special storage and handling requirements for different constituents should be considered on an individual basis, and the storage and handling of all samples to be analyzed should be documented in a field or laboratory notebook so that a sample handling history is maintained. This documentation should be done in accordance with QP-08.1.

See Section 6.3.3 for environmental control of samples during measurements.

Electrodes respond to the activity of ions, not their concentration. However electrodes will effectively respond to concentration if the ionic strength of all samples and standards is approximately the same (e.g., constant activity coefficients). The ionic strength will not be constant if the ion being measured (and/or its counterion) varies by more than an order of magnitude and is present in equal or greater concentration than all other ions in solution. In this case, it may be desirable to add a small amount of concentrated salt solution to the samples and standards so that the ionic strength of the solutions is dominated by the added salt and becomes approximately the same in all solutions. Recommended salts for ionic strength adjustment are usually discussed in the instruction manuals for ion-selective electrodes (some salts can interfere with the ion being measured). If the amount of salt solution added is significant relative to the sample size, the measured concentrations should be corrected for dilution. As a first approximation, ionic strength adjustment should not be necessary if the specific ion and its counterion never account for more than half the total ionic strength of the samples. Detailed information on the dependence of activity coefficients on ionic strength can be found in most advanced physical chemistry texts; for instance, "Electrolyte Solutions" by Robinson and Stokes.

**NOTE:** Calibration curves based on concentration can be prepared without maintaining a constant ionic strength, but these will not necessarily exhibit a linear electrode response with the logarithm of ion concentration, and they will be strictly valid only when the ionic strength of the unknowns varies in the same way as the ionic strength of the standards.

## 6.5 Implementing Procedure

### 6.5.1 Sample Analysis

The procedure for sample analysis will depend on the specific technique being used. This DP is intended to be general enough that it can be used for any of several techniques. The step-by-step procedure for any given technique should follow standard practice as described in the instruction manual for the ion-selective electrode or in another reference, such as an analytical chemistry text. Alternatively, the procedure can be determined by the PI. In either case, the step-by-step procedure should be documented. If standard practice is followed, documentation can be accomplished by referencing an existing document such as an instruction manual or textbook. However, it is advisable to photocopy and file all applicable pages in the existing document (including the title page and pages showing the copyright date, author, edition, etc..) to ensure future traceability.

All techniques have in common that an electrode response (voltage or voltage difference) must be recorded at some time. It is important that the electrode response be allowed to stabilize before a reading is recorded. Response time is typically longer in more dilute solutions and it can also depend on background ions. In some cases, it may be desirable to allow the same amount of time to elapse for each sample before recording a reading. If the response of a solid-state electrode becomes noticeably more sluggish with time, the tip should be polished with aluminum oxide polishing strips and the immersed in the most concentrated standard solution for about 5 minutes. Recalibration should be performed after polishing. Recalibration should also be performed approximately once every hour to check for electrode drift (see Section 6.3.2).

The electrodes and stirrers should be rinsed with deionized water and thoroughly blotted dry between measurements to avoid solution carryover from sample to sample. During measurements, direct contact between stirrers and electrode tips should be avoided. If a magnetic stirrer is used, it is advisable to place a layer of insulating material such as styrofoam between the sample container and the stirring plate so that heat transfer from the plate to the samples is minimized. As mentioned in Sections 6.3.3 and 6.4, all samples and standards should be kept at the same temperature or allowed to experience the same temperature conditions.

It is generally desirable to estimate the precision associated with a series of measurements. This is usually best accomplished by repeating measurements on a given sample several times over the course of all measurements so that a statistical measure of precision (e.g., standard deviation) can be estimated. If sample volumes severely restrict the



number of repeat measurements that can be made, then the repeat measurements should be made on a sample prepared from the standards (e.g., a dilution of one of the standards).

#### 6.5.2 Documentation of Results

Documentation requirements will depend on the technique used. Because it is not possible to foresee specific documentation requirements for all the ion-selective electrode techniques and their variations, the PI should determine the documentation requirements for each unique situation. In general, the user should record all measurements and calculations necessary to determine ion concentrations in the unknown. Some guidelines are given below for the various techniques.

For direct calibrations techniques, the following information should be recorded:

- Unique identifier of all equipment used for the measurements (e.g., manufacturer's name, model number, and serial number),
- any special sample preparation, such as ionic strength adjustment,
- measurements of electrode response associated with calibration standards (documentation of standard preparation for tracer concentration measurements should be done in accordance with DP-802 or in a field or laboratory notebook in accordance with QP-03.5),
- measurements of electrode response in unknowns, including repeat measurements to estimate analysis precision,
- temperature and stirring conditions of samples at times of measurement, and
- method of calculating concentrations of unknowns. For example, if calibration curves are used, a plot of each curve and the time of calibration should be recorded. As another example, the results of internal pH/voltmeter calibrations (e.g., slope fit parameter should be recorded.

For incremental or titration techniques (i.e., known addition, known subtraction, analyte addition, analyte subtraction), following information should be recorded:

- Unique identifier of all equipment used for the measurements (e.g., manufacturer's name, model number, and serial number),

- identity and concentrations of any reagents used (documentation of reagent preparation should be done in a field or laboratory notebook in accordance with QP-03.5),
- any special sample preparation, such as ionic strength adjustment,
- electrode responses associated with various amounts of reagent/unknown added or subtracted (incremental, titrations), and/or the amounts of reagent added when endpoints are reached (titrations),
- method(s) of calculating unknown concentrations.

## 6.6 Data Acquisition and Reduction

Data acquisition may be done manually or automatically, depending on the instrumentation and technique(s) used. When using direct calibration techniques, readings are converted to activities or concentrations using a calibration curve prepared according to the instruction manual for the ion-selective electrode. Information on preparing calibration curves is also available in general references such as the ORION Guide to Ion Analysis or analytical chemistry texts. Some pH/voltmeters have internal calibration features that allow voltage readings to be converted directly to concentrations that are displayed by the meter. However, there are often restrictions on the range of concentrations over which these internal calibration features can be used (e.g., only in the linear response region). When using incremental techniques or titrations, unknown concentrations are determined either from changes in the electrode response for a given amount of reagent added or subtracted (incremental techniques) or from the amount of reagent added when an endpoint is reached (titrations). The specific calculations involved with these methods should be described in the instruction manual for the ion-selective electrode or in more general references such as the ORION Guide to Ion Analysis or analytical chemistry texts. Depending on the technique, if ionic strength is not kept approximately constant in all samples and standards, it may be necessary to correct activities to concentrations using estimates of activity coefficients obtained from the literature (e.g., "Electrolyte Solutions" by Robinson and Stokes).

It is beyond the scope of this DP to describe all the calculations that could possibly be required when applying various ion-selective electrode techniques to determine ion concentrations in solution. However, for the special case of determining dilute ion concentrations (dilute enough that ionic strength corrections are not necessary) directly from electrode readings when the electrode responses associated with a more and a less concentrated standard are known, the following steps can be used (this is anticipated to be the most common application of this DP):

- Always be sure that a measurement associated with a more and a less concentrated standard is obtained both before and after the unknown is measured.
- If the electrode response for the standards is drifting, it is best to try to interpolate the standard responses associated with a given unknown reading by assuming that the drift is linear with time (or sample number). For example, if a standard had readings of -60.3 mV and -56.8 mV before and after an unknown is measured, respectively, and the unknown was the 4<sup>th</sup> of 10 samples measured between the two standard readings, then the proper standard reading to assume for the measurement of the unknown would be -60.3 + (4/10) (-56.8 - (-60.3)) = -58.9 mV. It has been found that precision can be improved if electrode drift is accounted for in this way.
- After obtaining the unknown reading (mV) and interpolated standard readings, the unknown concentration can be determined from the following equation:

$$C_U = C_L \left( \frac{C_H}{C_L} \right)^{\left( \frac{V_U - V_L}{V_H - V_L} \right)}$$

where,  $C_U$  = concentration of the unknown,  
 $C_L$  = concentration of less concentrated standard,  
 $C_H$  = concentration of more concentrated standard,  
 $V_U$  = potential (mV) of unknown,  
 $V_L$  = potential (mV) of less concentrated standard, and  
 $V_H$  = potential (mV) of more concentrated standard.

Data acceptance criteria cannot be established in this DP because the acceptance criteria will depend on the specific technique and instrumentation used. The PI reviews the data and associated records and determines the acceptability of the generated data. The PI may reject measurements for any of the following reasons:

- anomalous results
- unacceptably large standard deviations associated with repeat concentration measurements on the same sample, indicating poor measurement precision,
- operational deviations which call into question the accuracy of the results, and
- inadequate record keeping.

The identity of the rejected results and the basis for rejection are recorded in the field or laboratory notebook.

## 6.7 Potential Sources of Error and Uncertainty

Potential sources of error and uncertainty will depend on the specific technique used. However, whenever electrode responses are measured, the following sources of error and uncertainty may exist:

- temperature or stirring differences between samples,
- electrode drift between calibrations,
- reading the electrode response before it has stabilized (due to slow response),
- poor preparation of standards used for calibration,
- presence of interfering ions (i.e., ions that give an electrode response or that form complexes with the ion being measured) in the unknowns that are not present in the calibration standards, and
- failure to adjust all solutions to approximately the same ionic strength, or failure to correct for ionic strength differences.

When incremental or titration techniques are used, poor preparation of reagents used for addition or subtraction can also result in errors.

## 7.0 RECORDS

Records generated as a result of this DP are entries in field or laboratory notebooks or attachments to such notebooks. The documentation should consist of any applicable items identified in Section 6.0. Notebooks should be kept in accordance with QP-03.5.

All records should be submitted to the Records Processing Center in accordance with QP-17.6.

## 8.0 ACCEPTANCE CRITERIA

Proper completion and submittal of the records described in Section 7.0 constitutes the acceptance criteria for this procedure.

## 9.0 TRAINING REQUIREMENTS

Read only training is required for this DP. Training is documented in accordance with QP-02.7.

## 10.0 ATTACHMENTS

NA